

Control and Management for Direct Water Fuel Cell Systems

Chung-Hsing Chao¹, Jenn-Jong Shieh²

Department of Electrical Engineering, Ta Hwa Institute of Technology
Hsinchu, Taiwan.

¹davidee@thit.edu.tw, ²eesjj@et4.thit.edu.tw

Abstract—In this paper, the effectiveness analysis of direct water fuel cell systems including a fuel cell for hydrogen control and energy management by using magnesium hydrolysis reaction with a stainless steel catalyst inside the reactor is proposed. This study employed a Magnesium scraps and seawater to generate hydrogen gas. Metal catalyst was required for accelerating the reaction of H₂ generation in the Mg scraps/sea water solution. Purity of the generated H₂ was about 99%. The hydrogen energy systems included hydrogen storage of metal hydride to transfer the system's heat energy to the hydrogen storage and exit. The metal hydride not only recycled the heat energy from fuel cell but also averages the hydrogen supply of magnesium hydrolysis reaction which setup as a reactor. Experimental results prove that our prototype, can reach its hydrogen production efficiency by the chemical reaction about 97%. In this study, the user in on-demand period knows the data on the amount of hydrogen flow rate, the electricity from fuel cell, the temperatures of fuel cell, reactor, and metal hydride hydrogen storage, and recycled heat energy storage capacity information by the system interface. In the present study with no special hydrogen gas storage, fuel cells can be used directly to supply electricity.

Keywords—hydrogen generation control, hydrogen generation, energy systems, magnesium hydrolysis reaction

I. INTRODUCTION

Hydrogen has been identified as a promising energy carrier for the future because it offers the potential for fuel-efficient, emissions-free applications and can be produced from multiple primary energy sources. Utilizing clean hydrogen sources by fuel cell offers the potential to reduce greenhouse gas emissions and pollution. Nevertheless, many critical technical challenges need to be overcome before a hydrogen-based energy economy could become viable [1~5]. Hydrogen produced by chemical conversion of an energy source, can be used by the fuel cells to generate electricity to power devices. However, on-board hydrogen storage is one of the most challenging technical barriers to the implementation of the hydrogen economy. To achieve reasonable fuel efficiency and space-saving, weight and volume for on-board hydrogen storage system must be limited. As a result, the U.S. Department of Energy's Freedom Car Program targets [2] dictate that the gravimetric density of a hydrogen storage system should be at least 6 wt. % by weight, and the volumetric density should be at least 45 g H₂/litre by 2010. The targets for 2015 are 9 wt. % for gravimetric density and 81 g H₂/litre for volumetric density.

Existing hydrogen storage methods include compressed-hydrogen, liquid-hydrogen, metal-hydrides and chemical-

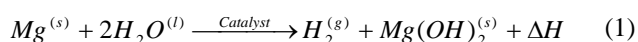
hydrides [3]. Sodium borohydride, also known as sodium tetrahydridoborate, is an inorganic compound with the formula NaBH₄ that finds wide applications and researches in hydrogen generation. This white solid, usually encountered as a powder, has attracted much attention because of their intrinsic safety and easy handling of fuel compared to other options [4~5]. This process is a famous method for hydrolysing to generation high-quality hydrogen gas without polluting emissions. However, one of shortcoming is the cost of sodium borohydride is too high, at around US\$ 80 dollars/kg [6]. The generation of hydrogen gas by the hydrolysis of high energy ball-milled magnesium-based materials in pure water and potassium chloride aqueous solution has been studied [7]. When the magnesium powders were milled for 0~10 hours, the hydrogen gas generation rate in 1 M potassium chloride aqueous was about 0.088~0.118 liter/min per one gram of Mg powders in 1 minute. And later the rate of generation hydrogen gas was reduced to the value of 0.00076~0.00882 litre/min in time period of 15~60 minute. Wang et al. [8] generated hydrogen gas from aluminium powders of 180~425µm in diameter in aqueous sodium hydroxide. The rate of hydrogen generation increased with reaction time up to 9 minutes, and beyond this time it started to decrease rapidly. Uan et al. [9] studied the possibility of generating hydrogen gas from low grade magnesium waste scraps. Only high grade magnesium scraps is being recycled and more than half of the remaining low grade magnesium scraps cannot be processed economically because the refining technology cannot clean the range of scrap produced. The experimental results [9] indicated that this method for generating hydrogen promotes the recycling of the end-of-life magnesium light alloy products. It is known that magnesium as an alkaline earth metal and the seventh most abundant element in the Earth's crust, where it constitutes about 2% by mass, and ninth in the known Universe as a whole. Due to magnesium ion's high solubility in water, it is the third most abundant element dissolved in seawater. As a result, magnesium scraps were considered commercially viable in the emerging fuel cell industry [10~11].

In the present study, it uses recycled magnesium as a source of hydrogen, electric and thermal energy are considered. It is known, that magnesium powders placed in sea-water solutions, decomposes water with formation of hydrogen and magnesium oxide or hydroxide, as well as plenty of heat. On the other hand, if in water solution any suitable electrode is placed together with magnesium, they form galvanic pair that is along with hydrogen generation such pair can serve as the electricity generator. Besides, magnesium is used in metal-air cells.

However, unstable for generating hydrogen gas can lead to fuel cell output current fluctuated. Insufficient chemical reaction of generating hydrogen and the formation of magnesium hydroxide can slow down fuel cell operation and performance in various ways, such as reducing output power or the effectiveness and thus obstructing the fuel cell output its electricity. Therefore, an effective, low-cost process for producing hydrogen and power generation is a basic requirement for commercializing fuel cells. The control and management for direct water fuel cell systems are discussed in the present study, and power characteristics of corresponding devices are also presented. Due to considerations of the cost and efficiency, pure magnesium or ball-milled powder is not considered here. Therefore, it uses the recycled magnesium scraps as a source of hydrogen for PEMFC. Prospects of new inexpensive technology of direct water fuel cell systems are analysed.

II. EXPERIMENT

The present study focused on the generation of hydrogen from recycled magnesium alloy scraps catalysed by a stainless steel net in an aqueous sodium chloride solution. This reaction of the corrosion of magnesium has been suggested to be catalysed herein by stainless steel net in sodium chloride solution to promote significantly the rate of generation of H₂. Therefore, the chemical reaction may be expressed as [9]



As shown in Fig. 1, magnesium scraps coupled with a stainless-steel-net catalyst were prepared to evaluate the ability of the hydrolysis reaction on improving H₂ yield in the explored aqueous solution.



Fig. 1 (a) magnesium-scrap (47grams by weight) coupled with stainless-steel-net (left) and the stainless-steel-net (20grams by weight) (right)

In this hydrolysis reaction, magnesium is the anode and the stainless steel net is the cathode during which molecules of water are split into hydrogen ions and hydroxide anions in the process of a chemical mechanism. The enthalpies of chemical

reaction was exothermic process by the value of $\Delta H = -353$ kJ/mole [9]. The by-product, magnesium hydroxide is a non-toxic compound, which is commonly used as flame retardant [9]. Additionally, the chloride ions attracted to the anode of magnesium are typically not oxidized to chloride gas because the half reaction occurs at a very noble potential below which the chloride ions is stable. Theoretically one gram magnesium can produce one litre of hydrogen at normal temperature and pressure of NTP, because the density of hydrogen is 0.084 kg/m³ at NTP [12]. According to the experimental results, the average cumulative volume of hydrogen generation was 27 litres by using 27.6 grams of magnesium as listed in Table 1. Therefore, in the present study the efficiency of hydrogen production by the chemical reaction was 97% at NTP.



Fig. 1 (b) the reaction products of magnesium hydroxyl in white powders

Fig. 2 shows data on the generation of hydrogen gas as a function of time. During the initial 0~120 seconds of the reaction, the average rate of H₂ generation increased to 0.9 litre per minute and then rapidly diminished to 0.4~0.2 litre/minute due to form an insulator of magnesium hydroxide with the formula Mg(OH)₂ which would hinder the catalyst to react continuously with magnesium scraps. The magnesium scraps were corroded easily via its high activity. However, if we put magnesium scraps in an aqueous sodium chloride solution,

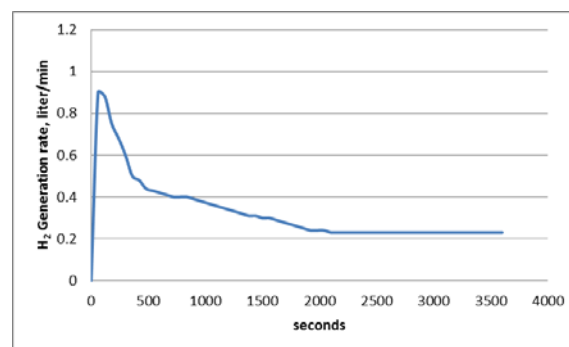


Fig. 2 hydrogen generation rate as a function of time

TABLE I MAGNESIUM SCRAP COUPLED WITH A STAINLESS-STEEL-NET CATALYST

Mg scraps sample No.	1	2	3	4	5	6	7	8	9	10	S.S. net weight	Mg scraps weight average
Mg scrap (including S.S. net)	48.2g	49.4g	39.1g	58.7g	49.8g	53.5g	54.6g	51.5g	33.8g	37.2g	20g	27.6g
Hydrogen generation in 10hours	1.0 L	1.1L	0.7L	1.4L	1.1L	1.2L	1.3L	1.1L	0.5L	0.6L	0L	1.0L

g: gram; L: litres

their surface of magnesium hydroxide should be destroyed and then corroded continuously. This corrosion for magnesium scraps in an aqueous solution generated hydrogen and magnesium hydroxyl. Magnesium scraps began to decompose into magnesium ion and electron as soon as contacting with water. If the aqueous solution contained a lot of hydrogen ion and then the electron would react with hydrogen ion to form hydrogen gas. As a result, magnesium scraps in an aqueous solution will generate magnesium ion, hydroxyl ion and hydrogen gas. As the corrosion proceeded it would consume hydrogen ion and generate hydroxyl ion. Noted that increased the concentration of hydroxyl would increase the PH value. If the PH value was more than 11.5, the magnesium ion would react with hydroxyl to form magnesium hydroxide as an insulator. Therefore, as shown in Fig. 2, the rate of hydrogen generation rapidly diminished after 120 seconds. The corrosion reaction will go forward in an aqueous solution unless the PH value is less than 8.5. Fig. 3 presents the cumulative volume of hydrogen generation versus time catalysed by stainless steel in an aqueous solution of 3.5 wt. % sodium chloride.

According to “metal hydride” as a buffer responded that the hydrogen supply for Mg scraps directly reacting in an aqueous sodium chloride solution catalysed by stainless steel has not been not on demand, may solve the problem which because the fuel cell under the variation of load cannot supply its power continuously. The effects of temperature for releasing hydrogen gas and hydrogen generation weight percentage are the main considerations with some metal hydrides [14]. The characteristics of these hydrides proved satisfactory for hydrogen storage, which needs the hydride to have the following properties including high hydrogen capacity, fast kinetics of hydrogenation and dehydrogenation, easy activation and minimal deterioration during hydrogenation cycling. Metal hydride which used as a buffer has excellent hydrogenation performance at ambient temperatures and hydrogen capacity typically in the range of 1~1.5 wt. % [13~15].

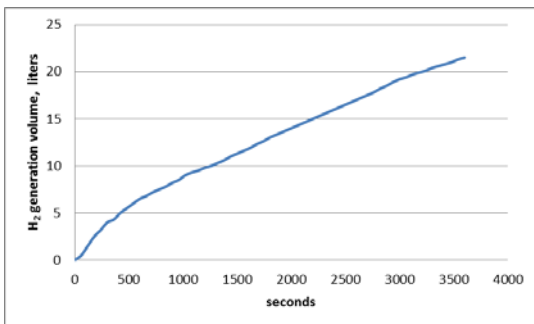


Fig. 3 cumulative volume of hydrogen generation as a function of time

III. PEM FUEL CELL

PEM fuel cell employs a thin polymer membrane as an electrolyte. The fuel cell needs a hydrogen pressure of minimum 1.2 bars to operate. Protons are the ionic charge carrier in a PEM fuel cell; the electrochemical reactions are corresponding to



It can be seen that the power and the efficiency of the PEM fuel cell. These calculations are based on considering a single

cell. The electric power of fuel cell stack P , efficiency η , hydrogen H_2 usage \dot{n}_h by using the unit mole/second of the mole flow rate and air usage \dot{n}_a of mole flow rate were theoretically calculated by [12]

$$P = V_c I_c N_c \quad (3)$$

$$\eta = \left(\frac{\mu_f V_c}{1.25} \right) \times 100\% \quad (4)$$

$$\dot{n}_h = \lambda \times \left(\frac{I_c N_c}{2F} \right) \quad (5)$$

$$\dot{n}_a = \lambda \times \left(\frac{I_c N_c}{0.21 \times 4F} \right) \quad (6)$$

where V_c is the cell voltage, I_c the cell current, N_c the number of cells, μ_f the fuel utilization (typically about 0.95), F the Faraday's constant (96498), λ the stoichiometry ratio 2.0 for hydrogen, and 1.25 the cell thermodynamic voltage which is the reversible thermodynamic cell voltage relative to the lower heating value (LHV). Because of the experiments in which water finally ends in liquid form were recycled for usage. According to the mole proportion of air, the mole ratio of oxygen is 0.21. In the present study, the fuel cell for cathode using air as reactant for the stoichiometry ratio 1.5 is operated below 100°C , so that liquid water is produced.

The linear relationship between the hydrogen molar flow rate \dot{n}_h used by the fuel cell and current I_c generated by the fuel cell is the sum of the reactor and metal hydride. As a result, a mass flow controller uses here for controlling the output power of fuel cell.

$$\dot{n}_h = \dot{n}_r + \dot{n}_m \quad (7)$$

In addition to the rate of usage of hydrogen, it is often also useful to know the electrical energy that could be produced from a given mass/mole or volume of hydrogen. It clearly follows that the difference between the actual cell voltage and this voltage represents the energy that is not converted into electricity because the energy that is converted into heat instead. The thermal power Q generated by the fuel cell is given the following equation

$$Q = P \left(\frac{1.25}{V_c} - 1 \right) \quad (8)$$

The specific enthalpy of hydrogen at LHV is $1.21 \times 10^8 \text{ J/kg}$ [12]. It also means that energy is leaving the fuel cell in three forms which are electricity, sensible heat and the latent heat of water vapour. Therefore the thermal power of sensible heat released from the fuel cell which is transferred partly to metal hydride hydrogen stocker and reactor, and the rest is transferred to the ambient environment. This relationship is denoted by,

$$Q = Q_m + Q_r + Q_a \quad (9)$$

In Eq. (9), Q_m is the rate energy exchange with metal hydride, Q_r the rate energy exchange with reactor, and Q_a the thermal power transferred between the fuel cell stack and the ambient environment according to

$$Q_m = hA(T_{fc} - T_m) \quad (10)$$

$$Q_r = hA(T_{fc} - T_r) \quad (11)$$

$$Q_a = hA(T_{fc} - T_a) \quad (12)$$

In these equations, T_{fc} , T_m , T_r and T_a are the temperatures for fuel cell, metal hydride, reactor, and ambient, respectively; h is the overall heat transfer coefficient of heat exchange and A the effective area of the heat transfer.

IV. DIRECT WATER FUEL CELL SYSTEMS

The experiment set up is carried on the hydrogen energy system as shown in Fig. 4 by recycling the fuel cell's heat energy to storage in the metal hydride canister in order to control hydrogen flow rate for transferring into electricity. The metal hydride hydrogen storage as a buffer not only recycles the heat energy from fuel cell but also averages the hydrogen supply when magnesium directly reacts with 3.5 wt. % sodium chloride solution catalysed by stainless-steel-net. As shown in Fig. 2, the rate of hydrogen generation increased in the initial stage of 0~120 seconds, and then reduced rapidly to 0.4~0.2 litre/minute. The excessive hydrogen coming from the chemical hydrides is amenable to be stored in a metal hydride and used afterwards to produce electricity by using the PEM fuel cell. Because the excessive hydrogen stored, it can be fed in the right stoichiometric ratio with oxygen by air.

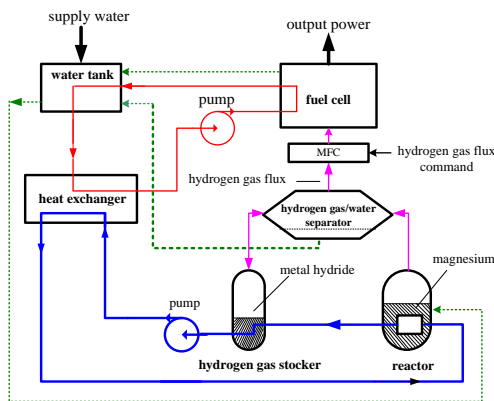


Fig. 4 setup of the proposed direct water fuel cell systems

The heat energy can be stored in metal hydride when the fuel cell discharges heat and the metal hydride emits immediately hydrogen gas on the absorption fuel cell heat energy to replenish the hydrogen gas which magnesium reacting in an aqueous sodium chloride solution catalysed by stainless steel net has insufficiency of the hydrogen supply. In contrast, the chemical hydride reactor produces excess the hydrogen supply when the load is reduced. As long as the hydrogen pressure is greater than that of metal hydride a bit, the hydrogen will enter metal hydride and simultaneously emit the quantity of heat energy. In this reversible process, the hydrogen has not been consumed but stored in metal hydride to constitute a heat energy accumulator together.

With the increasingly wide range of applications for hydrogen energy, the integrated heat and electrical energy of hydrogen energy systems not only employ a metal hydride hydrogen stocker as a buffer for recycling the heat energy but also control the input hydrogen flow rate by transferring

hydrogen into electricity. The integration of heat/electrical energy and metal hydride hydrogen storage enables a high efficiency hydrogen generation units located in a small volume to conduct on-demand monitoring with electricity power through a mass flow controller module, transmitting data back to computer. Considering the instability of hydrogen generation system for magnesium reacting in an aqueous sodium chloride solution catalysed stainless steel net, this study also added a metal hydride on the availability of controlling input hydrogen flow rate and recycling heat energy from the fuel cell.

V. RESULT AND DISCUSSION

The fuel cell stack was a 30W water-cooled PEMFC stack made by APFCT, and integrated by high efficiency micro heat pipes of heat exchangers. The nominal power was 30W at 60°C and 1.2 bars, with 10 cells and an active area of 25 cm². Air was supplied to stack by blowers, and hydrogen was supplied from the metal hydride canister 10 litres in the beginning until the stack's temperature over 60°C transferring heat energy to enhancement of the hydrogen generation together through a mass flow controller. The fuel cell stack temperature was controlled by a heat exchanger, additionally cooling water circulated with a small pump.

Fig. 4 shows the setup that integrates the chemical hydride reactor for hydrogen generation and metal hydride stocker as a buffer and a PEM fuel cell stack for output power. This figure also shows the water and heat energy balance between the PEM fuel cell stack, hydrogen gas stocker of metal hydride and reactor by a heat exchanger driven by circulating pumps. The chemical reaction that governs the hydrogen generation by reacting magnesium with water is given by Eq. (1).

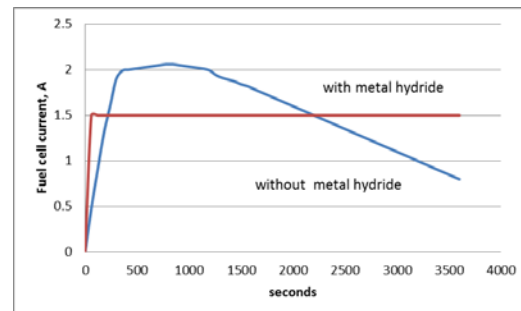


Fig. 5 fuel cell current under average 0.3 litre/minute hydrogen generation speed with/without metal hydrides

As shown in Fig. 5, the output current of fuel cell increased initially from zero to 2A in 3 minutes and remained in the range of 1.9~2.1A, and then decreased rapidly when the time over half an hour due to inadequate of hydrogen supply. During the same period, the output current of fuel cell was generated stably at the value of 1.5A with metal hydride. Such a generator can supply hydrogen fuel continuously and on-demand to the anodic compartment of a solid polymer fuel cell, even from ambient temperature and requiring only a small amount of power for pumping (less than 2W). The generator, consisting of a minimum of components, micro heat pipes of heat exchanger for example, is designed to minimize the overall volume and for an integration with a fuel cell into a power generator. Hydrogen generator works properly and its dynamic response and performance look adequate to be

coupled with a solid polymer fuel cell. Measured conversions for 97% are promising, and its proprietary catalyst shows a good chemical stability in the present study.

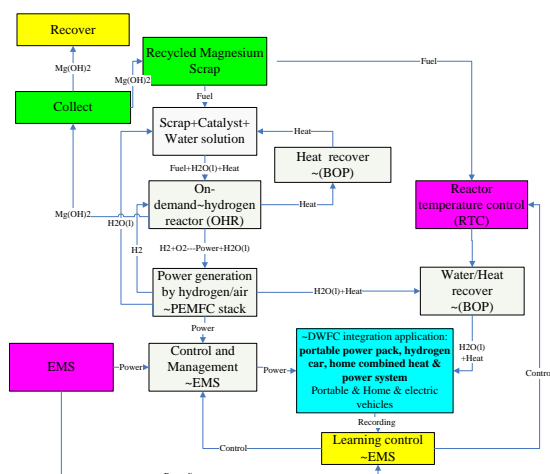


Fig. 6 the integration of hydrogen production and fuel cell power generation experimental concept map

As shown in Fig. 6, the integration of hydrogen generation and PEM fuel cell power generation experimental concept map to make hydrogen on-demand, combined with water and heat produced by PEMFC stack to control the reaction rate for hydrogen pressure maintained at a certain pressure (1.2~1.5bars), eliminating the need to store hydrogen and then pressurized to a high-pressure cylinders (250/500bars) or a low-temperature liquid hydrogen tank (-239.01 °C), can be directly connected to the fuel cell power generation system and stable output power, no longer hydrogen charging and releasing processes greatly by increasing the conversion efficiency which is a cost to make hydrogen and electricity conversion to be used in portable electronics power systems.

The present study developed by the integrated hydrogen and power for direct water fuel cell systems for control and management of hydrogen production in its preparation, is still unmatched in the way of industrialization and a large number of hydrogen (mainly gas based), if the supply of hydrogen towards miniaturization purposes (for example: notebook computers, portable phones, personal digital assistants and other low-power fuel cell) development, still has practical value. Main advantages of the hydrolysis reaction can be at any time and convenience while test piece is placed in sodium chloride aqueous solution of hydrogen production. In this study the hydrogen generator can be called real-time or on-demand hydrogen generator without the use of hydrogen storage by high pressured or liquid hydrogen production method to be the same appeal.

VI. CONCLUSIONS

The hydrogen energy systems not only recycles the heat energy from fuel cell but also averages the hydrogen supply of magnesium scraps directly reacting with water which setup as a reactor. Experimental results prove that our prototype, can reach its hydrogen production efficiency by the chemical reaction about 97%. In this study, we could show that the user in on-demand period knows the data on the amount of hydrogen flow rate, the electricity from fuel cell, the fuel

cell/reactor/metal hydride hydrogen storage temperature, and recycled heat energy storage capacity information by the system interface.

In the present study with no special hydrogen gas storage, fuel cells can be used directly to supply electricity. However, both methods require a large number of hydrogen through the hydrogen storage device storing gaseous or liquid hydrogen, so the way a lot of hydrogen and hydrogen storage devices and the overall security considerations will be more complex. In addition, the output without going through hydrogen purification, humidification process gas can be directly to the fuel cell for use. From the experimental results show that the production of hydrogen import to proton exchange fuel cell stack to convert it to electrical and heat energy forms.

ACKNOWLEDGMENT

This project is supported by the National Science Council of Taiwan under the grant no. of NSC-99-2221-E-233-006 and NSC 99-2632-E-233 -001-MY3.

REFERENCES

- [1] J. M. Ogden, M. M. Steinbugler, T. G. Kreutz., "A comparison of hydrogen, methanol and gasoline as fuels for fuel cell vehicles: implications for vehicle design and infrastructure development", J. Power Sources, vol.79 (2), pp.143-168, 1999.
- [2] A. Biyikoglu, "Review of proton exchange membrane fuel cell models", Int. J Hydrogen Energy, vol.30 (11), pp.1181-1212, 2005.
- [3] P. Ekdunge, M. Raberg, "The fuel vehicle analysis of energy use emissions and cost", Int. J. Hydrogen Energy, vol.23 (5), pp.381-385, 1998.
- [4] S. Prince Richard, M. Whale, N. Djilali, "A tech-economic analysis of decentralized electrolytic hydrogen production for fuel cell vehicles", Int. J Hydrogen Energy, vol.30 (11), pp.1159-1179, 2005.
- [5] M. L. Wald, "Questions about a hydrogen economy", Scientific American, vol.290 (5), pp.66-73, 2004.
- [6] S. C. Amendola, S. L. Sharp-Goldman, M. S. Janjua, M. T. Kelly, P. J. Petillo, M. Binder, "An ultrasafe hydrogen generator: aqueous, alkaline borohydride solutions and Ru catalyst", J. Power Sources, vol.85 (2), pp.186-189, 2000.
- [7] M. H. Grosjean, M. Zidoune, L. Roue, and J. Y. Huot, "Hydrogen production via hydrolysis reaction from ball milled Mg-based materials", Int. J. Hydrogen Energy, vol.31, pp.109-119, 2006.
- [8] H. Z. Wang, D. Y. C. Leung, M. K. H. Leung, M. Ni, "A review on hydrogen production using aluminium and aluminium alloys", Renewable and sustainable energy reviews, vol.13, pp.845-853, 2009.
- [9] J. Y. Uan, C.Y. Cho, and K. T. Liu, "Generation of hydrogen from magnesium alloy scraps catalyzed by platinum-coated titanium net in NaCl aqueous solution", Int. J. Hydrogen Energy, vol.32, pp.2337-2343, 2007.
- [10] G. Y. Moon, S. S. Lee, K. Y. Lee, S. H. Kim, K. H. Song, "Behavior of hydrogen evolution of aqueous sodium hydride solutions", J. of Industrial and Engineering Chemistry, vol.14, pp.94-99, 2008.
- [11] I. A. Taub, W. Roberts, S. LaGambina, and K. Kustin, "Mechanism of dihydrogen formation in the magnesium water reaction", J. Phys. Chem. A, vol.106, pp.8070-8078, 2002.
- [12] J. Larminie, A. Dicks, Fuel cell systems explained, Chichester, England, Wiley, pp.398, 2000.
- [13] I. A. Taub, W. Roberts, S. LaGambina, and K. Kustin, "Mechanism of dihydrogen formation in the magnesium water reaction", J. Phys. Chem. A, vol.106, pp.8070-8078, 2002.
- [14] T. Forde, J. Eriksen, A. G. Pettersen, P. J. S. Vie, O. Ulleberg, "Thermal integration of a metal hydride storage unit and a PEM fuel cell stack", Int. J. Hydrogen Energy, vol.34, pp.6730-6739, 2009.
- [15] G. Alefeld, J. Völkl (Eds.) : Hydrogen in Metals II, Springer-Verlag, Berlin, Heidelberg, New York, 1978